

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
25 January 2001 (25.01.2001)

PCT

(10) International Publication Number  
**WO 01/05886 A1**

(51) International Patent Classification<sup>7</sup>: C08K 5/06

(21) International Application Number: PCT/US00/18887

(22) International Filing Date: 12 July 2000 (12.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/144,507 19 July 1999 (19.07.1999) US

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/05886 A1

(54) Title: THERMALLY PROTECTIVE INTUMESCENT COMPOSITIONS

(57) Abstract: Novel intumescent compositions are disclosed having a component package for providing a char and char foam, a polymeric binder material and a crack control agent having 3-6 carbons and a boiling point in the range of 75-175 °C, the crack control agent having the structural formula  $R^2-O-CH_2-CR^1H-O-R^3$  wherein  $R^1 = -H$  or  $-CH_3$ ; and  $R^2$  and  $R^3$  independently comprise  $-H$ ,  $-R^4$ , or  $-COCH_3$ , wherein  $R^4 = C_1-C_3$  alkyl group. Further exemplary compositions comprise a polymer binder comprising a vinyl acetate/acrylate copolymer and a surfactant package with a dispersant. Methods of making and using the composition are also disclosed, as well as substrate packages incorporating the intumescent coating. One advantage of the intumescent coatings of the invention is the ability to prevent cracks in coatings which are spray-applied in relatively few passes, while achieving excellent fireproofing properties.

**THERMALLY PROTECTIVE INTUMESCENT COMPOSITIONS**

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**Field of the Invention**

The present invention relates to intumescent coatings, and more particularly to a novel intumescent coating composition providing excellent crack control and fireproofing performance.

**Background of the Invention**

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Intumescent coating compositions are well-known in the art. An outstanding feature of intumescent coatings is that they may be applied on substrates, such as metal, wood, plastics, graphite, and other materials, in the manner of a paint having relatively low film thickness. Upon exposure to fire, heat, or flames, the intumescent coatings, as their name implies, expand considerably in terms of thickness to produce an insulative layer of char and char foam.

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Numerous patents and publications have disclosed intumescent compositions containing one or more polymeric film-forming materials in combination with phosphate-containing materials and carbonific or carbon-yielding materials. *See e.g.*, US Patent 3,513,114 of Hahn et al.; US 5,487,946 of McGinniss et al.; US Patent 5,591,791 of Deogon; US Patent 5,723,515 of Gottfried; World Patent No. WO 94/17142 (PCT/US94/00643) of Buckingham; and World Patent No. WO 98/04639 (PCT/US96/12568) of Janci, all of which are incorporated fully herein by reference.

20

In U.S. Patent 3,513,114 assigned to Monsanto, Hahn et al. disclosed nearly 30 years ago that intumescent coating compositions can comprise an aqueous dispersion of a polyvinyl acetate-containing emulsion, a solvent plasticizer, and carbonific ammonium polyphosphates. In order to increase durability of their coatings, Hahn et al. taught the use of alkoxy glycol ethers having six to ten carbon atoms which were either partially or totally etherified and partially esterified by the substitution of an acetate group for one of the hydroxy groups. Examples of these included diethylene glycol monoethyl

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ether, diethylene glycol diethyl ether, ethylene glycol monoethyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether, 2-methoxy 2,4-dimethyl pentanediol 1, 5. Further, it was explained that alkoxy acetates which were suitable were ether chains having  
5 4-8 carbon atoms and were esterified by acetic acid (raising the total of carbon atoms to at least 6).

In US Patent 5,723,515 of Gottfried, it was taught to incorporate an elasticity agent, such as vermiculite, perlite, elastomerics, and acrylics, to increase resistance of the intumescent coating to cracking and shrinking and  
10 to improve ease of spraying.

The present inventors believe that a common problem of prior art intumescent coating compositions is that they must be applied using several successive coatings, for the most part on separate days, to prevent "cracking" in the coating layer. The ability of prior art intumescent formulations to  
15 obtain a sufficient coating thickness with relatively few spray passes, and the ability to obtain good fireproofing properties when such an intumescent coating is activated by heat or fire, remains elusive. The problem is that intumescent coatings, especially if applied in thick wet films, tend to crack and sag or flow downward due to gravity to form thickened portions which  
20 also have a tendency to crack. A similar cracking and/or sagging problem arises in detail areas, such as in corners.

Although fibers and fibrous materials can be incorporated into intumescent coatings to combat cracking, this approach often causes detrimental results in terms of aesthetic appearance, rheology, spray-ability,  
25 and/or hangability when the composition is spray-applied. Consequently, numerous separate coatings must be applied on different days, to achieve a sufficient and consistent coating thickness. The result is enhanced labor costs. Applying thick wet layers can be, in itself, a strong reason for cracks and failure due to the inability of the coating to expand or intumesce properly.

30 Thus, a novel intumescent coating composition is needed.

### Summary of the Invention

In surmounting the disadvantages of the prior art, the present invention provides an intumescent coating composition having excellent crack preventative behavior at high wet film thicknesses and fireproofing performance at minimal coating thicknesses. The coatings may be spray-applied, brushed, trowelled, or rolled, for example, using relatively few passes onto substrate surfaces, such as steel columns and beams; yet the coatings provide a protective carbonaceous char layer having excellent fire-retardant and thermal insulative properties when the coating is exposed to heat, fire, and/or flames.

An exemplary composition of the invention that intumesces upon activation by heat and/or fire, comprises: a component package for providing a char and char foam; a polymeric binder in emulsion form operative to form a film when the composition is allowed to dry; and a crack control agent having a total of 3 to 6 carbons and a boiling point in the range of 75-175°C., said crack control agent being represented by the structural formula



wherein  $\text{R}^1 = \text{-H}$  or  $\text{-CH}_3$ ; and  $\text{R}^2$  and  $\text{R}^3$  independently comprise  $\text{-H}$ ,  $\text{-R}^4$ , or  $\text{-COCH}_3$ , wherein  $\text{R}^4$  comprises a  $\text{C}_1\text{-C}_3$  alkyl group. A preferred crack control agent comprises alkoxy glycol ether, alkoxy glycol acetate, alkoxy glycol ether acetate, or mixtures thereof.

In further exemplary coatings, a surfactant package is employed comprising a nonionic alkylaryl polyether alcohol having the general formula  $\text{R}-\text{O}-(\text{OCH}_2\text{CH}_2)_x\text{OH}$ , wherein  $\text{R}$  is a  $\text{C}_4\text{-C}_8$  alkyl group (most preferably, a branched octyl group),  $\text{O}$  represents a phenylene group, and "x" represents an integer, preferably in the range of 15-100. Preferred surfactant packages may further comprise a dispersant, such as a polyacrylic acid or its salt (e.g., sodium polyacrylate) or derivatives.

The present invention also relates to processes for making and using the above-described intumescent coating composition; to methods for treating a substrate surface using the coating; and to substrates having the above-described intumescent coating composition. Further advantages and features  
5 of the present invention will be discussed in further detail hereinafter.

### Detailed Description of Exemplary Embodiments

Exemplary intumescent compositions are useful as coatings for protecting a variety of substrates from heat, fire, or flames. The substrates  
 5 may comprise metal, such as steel or aluminum columns, beams, joists, and panels, such as in construction or civil engineering surfaces; or such as in airplanes, automobiles, trucks, boats, trains, or other vehicles. The substrates which may be coated by compositions of the invention may also comprise, in addition to metal, other materials such as wood, plastic, composite materials  
 10 (e.g., graphite, fiberglass), glass, and others; and these may be in the form of fabric, cloth, felts, fibers, cables, sheets, boards, and films.

The compositions may be applied onto the substrate surface by any known means, such as by spray-application, dip-coating, brushing, trowelling, rolling, or other conventional means of application. For  
 15 fireproofing applications on steel columns and beams, spray-application is preferred for its labor- and time-saving advantages.

An exemplary intumescent composition of the present invention comprises a carbonaceous char-generating package for providing a char and char foam; a polymeric binder in emulsion form operative as a film-former  
 20 when dry; and a crack control agent having a total of 3 to 6 carbons and a boiling point in the range of 75-175°C., said crack control agent being represented by the structural formula



wherein  $\text{R}^1 = \text{-H}$  or  $\text{-CH}_3$ ; and  $\text{R}^2$  and  $\text{R}^3$  independently comprise  $\text{-H}$ ,  $\text{-R}^4$ , or  $\text{-COCH}_3$ , wherein  $\text{R}^4$  comprises a  $\text{C}_1\text{-C}_3$  alkyl group. A preferred crack control agent comprises alkoxy glycol ether, alkoxy glycol acetate, alkoxy glycol ether  
 30 acetate, or mixtures thereof. A particularly preferred crack control agent is propylene glycol monomethyl ether as will be described in further detail hereinafter.

An exemplary char-generating package for providing a carbonaceous char preferably comprises an acid source, a carbonific or carbon-yielding source, and optionally a blowing agent.

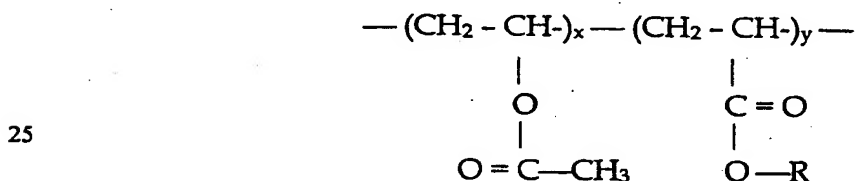
A preferred acid source contemplated for use in the present invention  
5 is an ammonium polyphosphate having repeating units having the formula  $(\text{PO}_3^- \bullet \text{NH}_4^+)_x$  wherein x is an integer between 1-3500, more preferably in the range of 150-2500, and most preferably within the range of 600-1200. Another preferred acid source is melamine (poly)phosphate. Other exemplary phosphate-containing materials useful as acid sources may include  
10 monoammonium orthophosphate, diamonium orthophosphate, condensed phosphoric acid, orthophosphoric acid, and the like. These may be thermally condensed with an ammoniating and condensing agent such as urea, ammonium carbonate, biuret, sulfamide, sulfamic acid, ammonium sulfamate, guanyl urea, methyl urea formamide amineo urea, 1-3-diamino urea, biurea  
15 and the like. For example, monoammonium orthophosphate and urea can be thermally condensed to prepare substantially water-insoluble ammonium polyphosphates by heat treating a melt formed from substantially equimolar quantities at a temperature of about 250°C for a period of about 3 hours. Generally, the ammonium polyphosphates can be employed in intumescent  
20 coatings in amounts of 10%-60%, more preferably 20%-50%, and most preferably 30%-40% based on the total weight of solids. Other known acid source materials commonly used in intumescent coating compositions may also be used in the present invention.

A preferred carbonific or carbon-yielding source suitable for use in the  
25 invention may include pentaerythritol,  $\text{C}(\text{CH}_2\text{OH})_4$ ; dipentaerythritol,  $\text{C}(\text{CH}_2\text{OH})_3-\text{O}-\text{C}(\text{CH}_2\text{OH})_3$ ; tripentaerythritol,  $\text{C}(\text{CH}_2\text{OH})_3-\text{O}-\text{C}(\text{CH}_2\text{OH})_2-\text{O}-\text{C}(\text{CH}_2\text{OH})_3$ ; or derivatives or mixtures thereof. Pentaerythritol is most preferred. The carbonific material may be employed in amounts of 2-40%; more preferably, 8-30%; and, most preferably, 10-20% by  
30 weight of total solids. Other carbonific materials conventionally used in intumescent coatings may also be used in the present invention. For

example, other carbonific materials may include an admixture or pre-formed products of resinous carbonifics such as urea and a source of formaldehyde such as paraformaldehyde, or urea-formaldehyde resins or melamine-formaldehyde resins. In addition, non-resinous carbonifics may be used  
 5 solely or in conjunction with the resinous carbonifics and which include carbohydrated, modified starches, and similar substances, a water-dispersible protein and a gelatin or casein or a polyhydric compound such as hexitols (mannitol), penitols (arabitol, monopentaerythritol, the poly-pentaerythritols, e.g., polymeric forms, as a dimer, trimer and the like).

10 Optionally but preferably, blowing agents may be used in the invention. A preferred blowing agent comprises melamine, urea, dicyandiamide, and mixtures thereof, which may be used in the amount of 1-25%, more preferably 5-20%, and most preferably 8-15% based on the weight of total solids in the coating composition. Other conventional blowing agents  
 15 believed to be suitable include components that are partly carbonific or carbon-yielding, as identified above, such as condensation products of formaldehyde and melamine, urea, and dicyandiamide. In this connection, guanidine, glycine, or a derivative or mixture thereof may also be used.

A preferred latex binder (e.g., used in emulsion form) contemplated for  
 20 use in the present invention comprises a vinyl acetate/alkyl acrylate copolymer having the formula



wherein R is a C<sub>1</sub> - C<sub>8</sub> alkyl group (more preferably, R is C<sub>4</sub>H<sub>9</sub>); and the ratio of x:y is in the range of 98:2 and 20:80. Preferably, the x:y ratio is between 95:5 and 50:50.

30 Two advantages of the preferred vinyl acetate/alkyl acrylate copolymer are its excellent compatibility with the char-generating components and, second, its stability with respect to high salt loadings. A



preferred level of the vinyl acetate/alkyl acrylate copolymer in the intumescent coating composition is 10-30%, and more preferably 15-25%, based on total dry weight of solids in the composition.

Another advantage of the preferred copolymer is that it does not shrink or crack when exposed to heat, fire, and/or flames, but softens just below the foaming temperature so that it does not interfere with the intumescent processes.

Other exemplary embodiments of the invention may comprise other polymer binders such as ethylene/vinyl acetate copolymer, and styrene/acrylate copolymers, among others.

Further exemplary coating compositions may comprise one or more pigments, such as titanium dioxide, zinc oxide, carbon black, iron oxide, or a mixture thereof. The pigments may be used in the amount of 5-25%, and more preferably 10-20%, based on total weight of solids in the composition.

Preferred intumescent coating compositions of the invention comprise a crack control agent having a total of 3 to 6 carbons and a boiling point in the range of 75-175°C., the crack control agent being represented by the structural formula



wherein  $\text{R}^1 = \text{-H}$  or  $\text{-CH}_3$ ; and  $\text{R}^2$  and  $\text{R}^3$  independently comprise  $\text{-H}$ ,  $\text{-R}^4$ , or  $\text{-COCH}_3$ , wherein  $\text{R}^4$  comprises a  $\text{C}_1\text{-C}_3$  alkyl group. Preferred crack control agent comprise alkoxy glycol ether, alkoxy glycol acetate, alkoxy glycol ether acetate, or mixtures thereof. Preferably, the crack control agent is water soluble. A preferred crack control agent is propylene glycol monomethyl ether having structural formula of  $\text{HOCH}_2\text{-C}(\text{CH}_3)\text{H-O-CH}_3$  and/or  $\text{CH}_3\text{-O-CH}_2\text{-C}(\text{CH}_3)\text{H-OH}$ .

Exemplary crack control agents of the invention thus comprise alkoxy glycol ether (e.g., ethylene glycol monomethyl ether having the formula  $\text{HO-}$

CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>3</sub> and ethylene glycol monoethyl ether having the formula HO-CH<sub>2</sub>-CH<sub>2</sub>-O-C<sub>2</sub>H<sub>5</sub>), alkoxy glycol acetate, and alkoxy glycol ether acetate; ethylene glycol monoacetate (HO-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-CH<sub>3</sub>) and propylene glycol monoacetate (HO-CH<sub>2</sub>-C(CH<sub>3</sub>)H-O-CO-CH<sub>3</sub> and/or CH<sub>3</sub>-CO-O-CH<sub>2</sub>-C(CH<sub>3</sub>)H-OH); ethylene glycol monomethyl ether monoacetate (CH<sub>3</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-O-CO-CH<sub>3</sub>), and propylene glycol monomethyl ether monoacetate (CH<sub>3</sub>-O-CH<sub>2</sub>-C(CH<sub>3</sub>)H-O-CO-CH<sub>3</sub> and/or CH<sub>3</sub>-CO-O-CH<sub>2</sub>-C(CH<sub>3</sub>)H-O-CH<sub>3</sub>). Mixtures of these crack control agents may be used.

Preferably, the crack control agent is used in an amount of 0.2-6.0%, more preferably 0.5-5.0%, and most preferably 1.0-4.0%, based on total dry solids in the composition.

In further exemplary intumescent coating compositions of the invention, a surfactant package is preferably incorporated. An exemplary component of such a surfactant package may comprise a nonionic alkylaryl polyether alcohol having the general formula R-Ø-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>x</sub>OH, wherein R is a C<sub>4</sub>-C<sub>8</sub> alkyl group (most preferably, a branched octyl group), Ø represents a phenylene group, and "x" represents an integer in the range of 15-100. More preferably, x is 30-70. This surfactant component may be used in the amount of 0.2-2.0% by weight of dry solids in the composition. A nonionic alkylaryl polyether alcohol which is suitable for use in the invention is commercially available from Union Carbide under the tradename TRITON (e.g., X-405, X-705).

Another component of the surfactant component, a component which works well in combination with the above-described polyether alcohol, is a dispersant which facilitates dispersion of solids in the aqueous environment. One exemplary dispersant comprises an acrylic acid (or its salt or derivative) such as sodium polyacrylic acid (or sodium polyacrylate in its salt form), which is commercially available from Rohn & Haas under the tradename Tamol®. Preferably, the dispersant used is water-soluble. The dispersant

may be used in the amount of 0.5-3.0%, and more preferably in the range of about 0.7-1.5%, based on total solids in the composition.

It is also contemplated that rheology modifiers can be incorporated into compositions of the invention. Exemplary rheology modifiers include  
5 xanthum gum, carboxylated xanthum gum, cellulose ethers such as carbomethoxy cellulose, methyl cellulose, and hydroxy cellulose; stratified silicates such as montmorillinite, bentonite, hectorite, and attapulgite.

Further exemplary components may include additives that are conventionally used for intumescent coating compositions, such as pH  
10 adjustors; biocides (including fungicides and bactericides); deagglomeraters; processing aids (such as clays, medium or fine particle solids, organic solvents, alcohols, or waxes); fibers (such as glass, polymer, Wollastonite); and fillers. A pH adjustor in this case would be used to neutralize the acid environment caused by the acid source, and thus increase the pH to around or  
15 above 7, and this would also increase the efficacy of the dispersant. An exemplary pH adjustor is ammonia or sodium hydroxide. Other base materials would also likely work. Biocides (including fungicides and bactericides) are also optional in the exemplary intumescent coatings of the invention, but in this case they are preferable to use because they would help  
20 to preserve the integrity of the coating and its ability to intumesce when needed. Such further additives can be used in varying amounts as would be known without undue experimentation by those skilled in the art upon viewing the present disclosure.

The invention also relates to structures having the above-described  
25 composition coated over the surface of the structure. Preferred embodiments include metal structures, such as steel columns or panels, having a spray-applied coating of the above-described intumescent composition in (approximate) thicknesses of 0.1-6.0mm, and more preferably 0.2-4.0 mm. Exemplary methods of the invention for applying the afore-mentioned  
30 coating compositions comprise spray-applying onto a substrate surface.

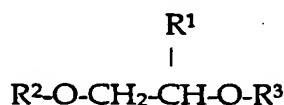
A preferred method of protecting a substrate with an intumescent fire-retarding coating comprises spray-applying the above-described intumescent composition in one pass on the substrate surface whereby a wet coating layer thickness of 0.5-5.0 mm is formed, and allowing said wet coating layer to dry.

- 5 Preferred wet coating layers are 1-3 mm, and, when dry, provide a dry coating layer thickness of approximately 0.7-2.0 mm. Preferably, such coating layer thicknesses are obtained in one spraying pass.

- One advantage of the present invention is that the intumescent coating may be applied in relatively few passes and possess, nevertheless, excellent  
10 fireproofing capabilities. In its product form, the coating composition may be used with a compatible primer and topcoat. The purpose of a primer is to enhance adhesion of the intumescent coating to the substrate, and the purpose of the topcoat is to provide a decorative appearance (e.g., color, gloss) or to enhance durability of the coating. These are commercially available and are  
15 known in the fireproofing industry.

- Intumescent coating compositions of the invention may be formulated using conventional thickeners and various water amounts, such as to provide a paste or even less fluid form that would be useful for a solid firestop article (e.g., board, panel). However, another advantage of the inventive coating  
20 compositions taught herein is to provide a highly effective spray-applicable coating composition that prevents cracking in relatively high wet layer thicknesses.

- The invention also provides a process for preventing cracking in an intumescent coating, comprising combining a polymeric latex binder, a  
25 component package for providing a char and char foam (such as an acid source, a carbonific or carbon-yielding source), and a crack control agent having a total of 3-6 carbons and a boiling point in the range of 75-175°C., said crack control agent being represented by the structural formula



30

wherein  $R^1 = -H$  or  $-CH_3$ ; and  $R^2$  and  $R^3$  independently comprise  $-H$ ,  $-R^4$ , or  $-COCH_3$ , wherein  $R^4$  comprises a  $C_1$ - $C_3$  alkyl group. Preferred crack control agent comprise alkoxy glycol ether, alkoxy glycol acetate, alkoxy glycol ether acetate, or mixtures thereof. Preferably, the crack control agent is water soluble. A preferred crack control agent is propylene glycol monomethyl ether having structural formula of  $HOCH_2-C(CH_3)H-O-CH_3$  and/or  $CH_3-O-CH_2-C(CH_3)H-OH$ .

Exemplary processes also includes incorporating the exemplary latex binder described above, and further exemplary processes include incorporating one or more of the preferred surfactant package components into the coating composition, as described above.

### Example 1

Coating compositions, using exemplary crack control agents of the present invention, namely, ethylene glycol monomethyl ether and propylene glycol monomethyl ether, were prepared in batch sizes of 15 Kg to 20 Kg using a mixer equipped with a high speed dispersion blade and a slow scrapper blade. Each material was mixed until thoroughly dispersed before adding the next ingredient. Mixing speeds were varied throughout the blending process to achieve optimum dispersion. When completely blended, the formulations were stored in an airtight non-metallic container.

Table 1

| <u>Material</u>                   | <u>Example 1</u><br>(part by weight) | <u>Example 2</u><br>(part by weight) |
|-----------------------------------|--------------------------------------|--------------------------------------|
| Water                             | 25-35                                | 25-35                                |
| Ethylene glycol monomethyl ether  | 1-3                                  | 0                                    |
| Propylene glycol monomethyl ether | 0                                    | 1-3                                  |
| Potassium tripolyphosphate        | 0.2-0.5                              | 0.2-0.5                              |
| Carboxylated xanthum gum          | 0.05-0.15                            | 0.05-0.15                            |
| Ammonium hydroxide                | 0.4-0.6                              | 0.4-0.6                              |
| Ammonium polyphosphate            | 22-28                                | 22-28                                |
| Pentaerythritol                   | 8-12                                 | 8-12                                 |
| Melamine                          | 7-11                                 | 7-11                                 |

|   |           |           |
|---|-----------|-----------|
| Titanium dioxide                            | 8-14      | 8-14      |
| Triton (Union Carbide Tradename)            | 0.2-1.5   | 0.2-1.5   |
| Tamol (Rohm and Haas Tradename)             | 1.5-3.0   | 1.5-3.0   |
| Proxel (Tradename of )                      | 0.03-0.07 | 0.03-0.07 |
| Resyn latex Tradename of Nacan Ltd., Canada | 18-24     | 18-24     |

5        The effectiveness of the crack control agents was evaluated in a spraying test. In this test, a galvanized steel plate of 10-inch by 10-inch was bent at the center to form a curved right angle wherein the curved corner had a radius of 0.5 inches. The bent plate was coated with a primer and dried thoroughly. The intumescent formulation was then sprayed onto these plates  
10    to achieve three different wet coating thicknesses of 0.8, 1.0, and 1.3 mm. The coated plates were allowed to dry at ambient conditions. In general, cracking occurs, during drying process, much more at the corners than on the flat surface and also increases with increasing thickness of the coating. A good crack control agent inhibits cracks both on the planes and at the corners for  
15    coatings up to 1.3 mm wet thickness. The results of the spraying test of these formulations are shown in Table 2.

For evaluation of fire proofing performance, the intumescent formulation was sprayed onto 10-inch by 10-inch by 1/4-inch steel plates to  
20    form a uniform dry coating with a thickness of 1.50~1.60 mm. After cured, the coated plate was exposed to a standard ASTM E-119 simulated fire. Such a fire simulation involves the use of a flame whose temperature is continuously increased to 927°C during a one-hour period. The temperature of the steel plate is also continuously monitored and recorded. The average  
25    temperature reached after one-hour exposure to ASTM E-119 simulated fire was used to compare the efficiency of the intumescent coating. The lower temperature indicates a more effective insulation and a better fire proofing performance. The results of the fire test are also shown in Table 2.

**Table 2**

|                       | <b>Example 1</b>   | <b>Example 2</b> |
|-----------------------|--|------------------|
| Wet coating thickness | Appearance of dried coating at corners   |                  |
| 0.8 mm                | No crack   | No crack         |
| 1.0 mm                | No crack   | No crack         |
| 1.3 mm                | No crack   | No crack         |
| Dry coating thickness | Temperature (°C) of steel plate after exposed to fire for 1 hour <sup>1)</sup> |                  |
| 1.50 ~ 1.60 mm        | 275 - 325  | 275 - 325        |

<sup>1)</sup> According to ASTM E119

As shown in Table 2, the crack control agents of the invention clearly show excellent performance in terms of avoiding cracks and improving fire-proofing properties.

5

### **Examples 3 and 4**

*(Prior Art - Comparative)*

The comparative compositions of Examples 3 and 4 are shown in Table 3 and were prepared using similar general procedure of Examples 1 and 2.

10

**Table 3**

| <b>Material</b>                              | <b>Example 3</b><br>(part by weight) | <b>Example 4</b><br>(part by weight) |
|--|--------------------------------------|--------------------------------------|
| Water  | 25-35                                | 25-35                                |
| Diethylene glycol monobutyl ether            | 1-3                                  | 0                                    |
| Dipropylene glycol monomethyl ether          | 0                                    | 1-3                                  |
| Potassium tripolyphosphate                   | 0.2-0.5                              | 0.2-0.5                              |
| Xanthum gum                                  | 0.05-0.15                            | 0.05-0.15                            |
| Ammonium hydroxide                           | 0.4-0.6                              | 0.4-0.6                              |
| Ammonium polyphosphate                       | 22-28                                | 22-28                                |
| Pentaerythritol                              | 8-12                                 | 8-12                                 |
| Melamine                                     | 7-11                                 | 7-11                                 |
| Titanium dioxide                             | 8-14                                 | 8-14                                 |
| Triton (Tradename of Union Carbide)          | 0.2-1.5                              | 0.2-1.5                              |
| Tamol (Tradename of Rohm and Haas)           | 1.5-3.0                              | 1.5-3.0                              |
| Proxel (Tradename of Zeneca)                 | 0.03-0.07                            | 0.03-0.07                            |
| Resyn latex (Tradename of Nacan Ltd, Canada) | 18-24                                | 18-24                                |

In Examples 3 and 4, diethylene glycol monobutyl ether and dipropylene glycol monomethyl ether were substituted, respectively, in place of the crack control agents of the invention. These two substituted ingredients were described in US Patent 3,513,114 (Hahn et al.). Both formulations showed a similar visual appearance from that of Examples 1 or 2, but the similarities ended here.

The spraying characteristics and fire proofing properties of these formulations were also evaluated and the results are summarized in Table 4.

| <b>Table 4</b>        |  |                  |
|-----------------------|--|------------------|
|                       | (Prior Art)  | (Prior Art)      |
|                       | <b>Example 3</b>   | <b>Example 4</b> |
| Wet coating thickness | Appearance of dried coating at corners   |                  |
| 0.8 mm                | No crack   | No crack         |
| 1.0 mm                | Minor cracks   | Cracks           |
| 1.3 mm                | Severe cracks  | Severe cracks    |
| Dry coating thickness | Temperature (°C) of steel plate after exposed to fire for 1 hour <sup>1)</sup> |                  |
| 1.50 ~ 1.60 mm        | 340-380  | 420-470          |

<sup>1)</sup> According to ASTM E119

The results in this table clearly indicate inferior properties of these formulations because they demonstrated cracking (severe at thicker coatings) and decreased fireproofing capability in contrast to the Examples 1 and 2 above which employed exemplary crack control agents of the present invention.

#### **Examples 5 and 6**

*(Comparative)*

For comparative purposes, two additional formulations (Examples 5 and 6) were also prepared in the same manner. Example 5 employed a



widely used water-soluble ethylene glycol while Example 6 utilized a widely used oil-soluble Texanol® instead of the crack control agent of the invention.

**Table 5** (comparative) (comparative)

| Material                                     | <u>Example 5</u><br>(part by weight) | <u>Example 6</u><br>(part by weight) |
|--|--------------------------------------|--------------------------------------|
| Water  | 25-35                                | 25-35                                |
| Ethylene glycol                              | 1-3                                  | 0                                    |
| Texanol (Tradename of Eastman Chemicals)     | 0                                    | 1-3                                  |
| Potassium tripolyphosphate                   | 0.2-0.5                              | 0.2-0.5                              |
| Xanthum gum                                  | 0.05-0.15                            | 0.05-0.15                            |
| Ammonium hydroxide                           | 0.4-0.6                              | 0.4-0.6                              |
| Ammonium polyphosphate                       | 22-28                                | 22-28                                |
| Pentaerythritol                              | 8-12                                 | 8-12                                 |
| Melamine                                     | 7-11                                 | 7-11                                 |
| Titanium dioxide                             | 8-14                                 | 8-14                                 |
| Triton (Tradename of Union Carbide)          | 0.2-1.5                              | 0.2-1.5                              |
| Tamol (Tradename of Rohm and Haas)           | 1.5-3.0                              | 1.5-3.0                              |
| Proxel (Tradename of Zeneca)                 | 0.03-0.07                            | 0.03-0.07                            |
| Resyn latex (Tradename of Nacan Ltd, Canada) | 18-24                                | 18-24                                |

5

The spraying characteristics and fireproofing properties of these formulations were also evaluated and the results summarized in Table 6 below.

10

**Table 6** (comparative) (comparative)

|                       | <u>Example 5</u>   | <u>Example 6</u> |
|-----------------------|--|------------------|
| Wet coating thickness | Appearance of dried coating at corners                                       |                  |
| 0.8 mm                | No crack   | Some cracks      |
| 1.0 mm                | Some cracks  | Severe cracks    |
| 1.3 mm                | Severe cracks  | Severe cracks    |
| Dry coating thickness | Temperature (°C) of steel plate after exposed to fire for 1 hour (ASTM E119) |                  |
| 1.50 ~ 1.60 mm        | 750-780  | 370-420          |

The results in this table clearly indicate inferior properties of these formulations because they evidenced cracking and decreased fireproofing  
5 capability in contrast to the Examples 1 and 2 above.

The foregoing description and examples are intended for illustrative purposes only and not intended to limit the scope of the invention.

*It is claimed:*

1. A composition that intumesces upon activation by heat or fire, comprising: a component package for providing a char and char foam; a polymeric binder in emulsion form operative when dry to form a film; and a crack control agent comprising having a total of 3 to 6 carbons and a boiling point in the range of 75-175°C., said crack control agent being represented by the structural formula

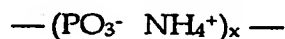


wherein  $\text{R}^1 = -\text{H}$  or  $-\text{CH}_3$ ; and  $\text{R}^2$  and  $\text{R}^3$  independently comprise  $-\text{H}$ ,  $-\text{R}^4$ , or  $-\text{COCH}_3$ , wherein  $\text{R}^4$  comprises a  $\text{C}_1\text{-C}_3$  alkyl group.

2. The composition of claim 1 wherein said component package for providing a char and char foam comprises an acid source and a carbonific or carbon-yielding source.

3. The composition of claim 2 further comprising a blowing agent.

4. The composition of claim 2 wherein said acid source comprises an ammonium polyphosphate comprising repeating units having the formula



wherein  $x$  is an integer of 2-3500.

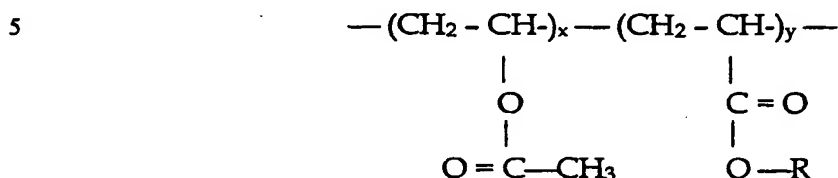
5. The composition of claim 2 wherein said carbonific or carbon-yielding source comprises a pentaerythritol, dipentaerythritol, tripentaerythritol, or mixtures thereof.

6. The composition of claim 3 wherein said blowing agent comprises a melamine.

7. The composition of claim 1 wherein said polymeric base material comprises a polymer selected from vinyl acetate/alkyl acrylate, ethylene/vinyl acetate, styrene/alkyl acrylate, or mixture thereof.

8. The composition of claim 7 wherein said polymer comprises a vinyl acetate/alkyl acrylate copolymer.

9. The composition of claim 8 wherein said copolymer has the formula



10 wherein R is a C<sub>2</sub> - C<sub>8</sub> alkyl; and the ratio of x:y is in the range of 98:2 to 20:80.

10. The composition of claim 7 wherein R is C<sub>4</sub>H<sub>9</sub>.

11. The composition of claim 1 wherein said crack control agent comprises an alkoxy glycol ether, an alkoxy glycol acetate, an alkoxy glycol ether acetate, an ethylene glycol monoacetate, a propylene glycol monoacetate, an ethylene glycol monomethyl ether monoacetate, a propylene glycol monomethyl ether monoacetate, or mixtures thereof.

12. The composition of claim 11 wherein said crack control agent comprises propylene glycol monomethyl ether, an ethylene glycol monomethyl ether, an ethylene glycol monoethyl ether, or mixtures thereof.

13. The composition of claim 11 wherein said crack control agent comprises an ethylene glycol monomethyl ether having the formula HO-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>3</sub>, an ethylene glycol monoethyl ether having the formula HO-CH<sub>2</sub>-CH<sub>2</sub>-O-C<sub>2</sub>H<sub>5</sub>, or mixtures thereof.

14. The composition of claim 11 wherein said crack control agent comprises propylene glycol monomethyl ether.

15. The composition of claim 1 further comprising a surfactant package.

16. The composition of claim 15 wherein said surfactant package comprises a nonionic alkylaryl polyether alcohol having the general formula R-Ø-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>x</sub>OH, wherein R is a C<sub>4</sub>-C<sub>8</sub> alkyl group (most preferably, a

branched octyl group), Ø represents a phenol group, and "x" represents an integer in the range of 15-100.

17. The composition of claim 16 wherein x is 30-70.

18. The composition of claim 15 wherein said surfactant package  
5 further comprises a dispersant comprising a sodium polyacrylic acid or its salt or derivative.

19. The composition of claim 1 further comprising a rheology modifier comprising xanthum gum, carboxylated xanthum gum, a cellulose ethers, hydroxy cellulose, a stratified silicate, or a mixture thereof.

10 20. The composition of claim 1 further comprising carboxylated xanthum gum.

21. The composition of claim 1 further comprising a biocide, fungicide, anti-bacterial agent, or mixture thereof.

22. The composition of claim 1 further comprising a base material  
15 that is operative to decrease the acidity of said composition.

23. The composition of claim 1 wherein said acid source comprises an ammonium polyphosphate; said carbonific or carbon-yielding source comprises a pentaerythritol, dipentaerythritol, or mixture thereof; said polymeric base material comprises vinyl acetate/acrylate copolymer; said  
20 crack control agent comprising propylene glycol monomethyl ether; and said composition further comprises surfactant package comprising a nonionic alkylaryl polyether alcohol and a dispersant.

24. The composition of claim 22 wherein said nonionic alkylaryl polyether alcohol has the general formula  $R-\text{Ø}-(\text{OCH}_2\text{CH}_2)_x\text{OH}$ , wherein R  
25 is a  $\text{C}_4\text{-C}_8$  alkyl group, Ø represents a phenol group, and "x" represents an integer in the range of 15-200.

25. The composition of claim 24 wherein said surfactant package further comprises a dispersant comprising a sodium polyacrylic acid or its salt or derivative.

30 26. Process comprising applying to the surface of a substrate the composition of claim 1.

27. The process of claim 26 wherein said substrate comprises a metal, plastic, wood, composite, glass, or a mixture thereof.

28. An article comprising a substrate having a surface coated with the composition of claim 1.

5 29. Process for preventing cracking in an intumescent coating, comprising combining a polymeric latex binder, an acid source, a carbonific or carbon-yielding source, and a crack control agent having 3 to 6 carbons and having a boiling point in the range of 75-175°C., said crack control agent being represented by the structural formula



wherein  $\text{R}^1 = \text{-H}$  or  $\text{-CH}_3$ ; and  $\text{R}^2$  and  $\text{R}^3$  independently comprise  $\text{-H}$ ,  $\text{-R}^4$ , or  $\text{-COCH}_3$ , wherein  $\text{R}^4$  comprises a  $\text{C}_1\text{-C}_3$  alkyl group.

15

30. The process of claim 29 wherein said crack control agent comprises propylene glycol monomethyl ether.

31. The process of claim 30 wherein said propylene glycol monomethyl ether is water-soluble.

20 32. The process of claim 31 wherein said ether is esterified with an acetate group.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/18887

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : CO8K 5/06

US CL : 106/18.18; 523/179; 524/ 306, 317, 376, 377, 378 415,416.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/18.18; 523/179; 524/ 306, 317, 376, 377, 378 415,416.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
"Paint Additives 1970" ed. Harold Preuss (1970), Noyes Data Corp. Pub.Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
East and West**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category*    | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.         |
|--------------|---|-------------------------------|
| X<br>--<br>Y | US 3,513,114 A [HAHN et al] 19 May 1970, see. col.7, ex. III, lines 40-65   | 1-9,15,26-29<br>-----<br>1-32 |
| Y            | US 4,552,908 A [NICKS et al] 12 November 1985,col.3, lines 28-58  | 1-32                          |
| Y            | US 4,914,142 A [TAKARABE et al] 03 April 1990, col.3, lines 20-60; col.5, lines 35-44; col.6, lines 58-64; col.7, lines 16-21 | 1-17,21,26-32                 |
| Y            | PRUESS, HAROLD: PAINT ADDITIVES 1970, pages 74-82,100-106 and 176, Noyes Data Corp. Park Ridge , New Jersey (1970)            | 1-10,15-23,25-29              |

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

|   |  |
|---|--|
| * Special categories of cited documents:  | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  |
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| "E" earlier document published on or after the international filing date  | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "&" document member of the same patent family  |
| "O" document referring to an oral disclosure, use, exhibition or other means  |  |
| "P" document published prior to the international filing date but later than the priority date claimed  |  |

Date of the actual completion of the international search

20 SEPTEMBER 2000

Date of mailing of the international search report

19 OCT 2000

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